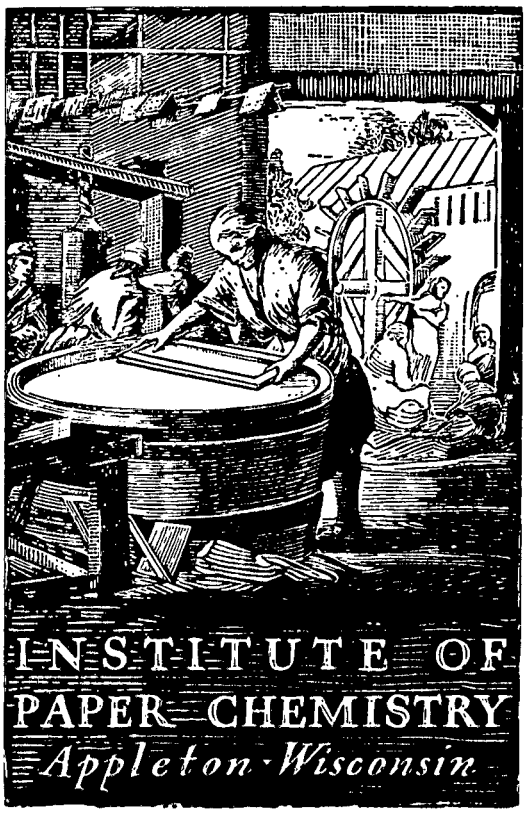

DEVELOPMENT AND APPLICATION OF ANALYTICAL TECHNIQUES

YIELD DETERMINATIONS IN CONTINUOUS DIGESTERS

Project 3477-2

Report One
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

January 23, 1981

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

A method for using carbohydrate analyses for estimation of pulp yields is being evaluated. The method depends on the assumption that the yield of cellulose as percentage of a particular wood species is essentially constant in a kraft cook. Prior to use of the method, the yield of cellulose from each wood species being pulped is normally determined in the laboratory.

Replicate analyses of the carbohydrates in a laboratory-prepared kraft pulp have been performed. Data from these analyses have been used in calculating estimated yields. The data appear to be sufficiently precise to distinguish between pulps having yields differing by about 1%.

Pulping yield estimates by two methods which utilize carbohydrate analyses have been compared. Improved precision resulted from the procedure which employs independent measurement of lignin as well as carbohydrates in the pulp.

A single sample of derivatized carbohydrates was repetitively injected into the gas chromatograph. Results suggest that gas chromatography contributed significantly to the variation of the carbohydrate analysis. Accuracy and precision of the analysis should be enhanced by adoption of a standard pulp for calibration and by use of specific pieces of equipment and techniques found to be of value in the method.

INTRODUCTION

One measure of pulp mill performance is pulping yield, the amount of pulp produced from a given quantity of wood consumed. Inventory measurements provide an indication of yield over an extended period of time. However, inventory data are insensitive to yield changes occurring for brief periods, such as when pulping process modifications are being evaluated.

In mills with batch digesters, capsules or baskets suspended in the digester may be used for yield determinations. The weight of pulp produced from the known weight of chips in the capsule is determined. This assumes that the pulping of the chips in the capsule is representative of that occurring in the rest of the digester.

Because capsule cooks are not possible in mills having continuous digesters, indirect methods must be used for yield estimation. One such method, based upon carbohydrate determinations, depends upon the assumption that the yield of cellulose (% on o.d. wood) is essentially constant in a normal kraft cook. In this procedure pulp yield is computed from the following expression:

$$100(Y\ cell/C) = Y_t \qquad (1)$$

where $Y\ cell$ = yield of cellulose, % on o.d. wood,

C = cellulose content, % on o.d. pulp, and

Y_t = yield of pulp, % on o.d. wood.

Y cell is determined from laboratory cooks in which wood and pulp are accurately weighed. Cellulose contents are measured by the gas chromatographic procedure for carbohydrates developed by Borchardt and Piper at the Institute in 1970 (1,2).

Variations on Eq. (1), in which carbohydrate yield and lignin yield are determined separately, have also been used with success.

Because a viable method of yield determination will have wide applicability, a thorough evaluation of the carbohydrate method of yield estimation will be made. If successful, the technique will provide a way to follow carbohydrate yield independent of lignin as well as to estimate overall pulp yield. This will be useful in studies of optimization procedures to minimize carbohydrate loss independent of lignin levels. Included in the evaluation will be a study of the accuracy and precision of the method for carbohydrate determination and testing of the assumptions used in converting the measured carbohydrate values into yield figures.

USE OF CARBOHYDRATE DETERMINATION FOR YIELD ESTIMATION

Figure 1, copied from Rydholm's Pulping Processes (3), illustrates that cellulose yield varies little during kraft pulping. From a series of laboratory cooks of slash pine, Matthews has shown that cellulose yield, expressed as a percentage of the wood, remained essentially constant at 37.3% over a pulping yield range from 49.7 to 68.7% (4). Cellulose was determined by gas chromatography (5); it is the total glucose content of the pulp corrected for the glucose present in the galactoglucomannan (1 glucose per 3 mannose units in softwood pulp). Similar results have been obtained on loblolly pine at the Institute (6) and are shown in Table I. Cellulose in the pulp, expressed as percentage of wood, remained constant at approximately 36% for 8 hours after the cooking temperature had been reached. A nearly constant value of 39% was obtained in another recent study in which kraft-anthraquinone pulps were prepared over a wide yield range (7). As described below, the approximately constant yield of cellulose from wood provides the basis for use of carbohydrate data for pulping yield estimation.

That yield in continuous digesters could be estimated from carbohydrate analysis results was apparently first implied by Rydholm in Continuous Pulping Processes (8). In Rydholm's (Billeruds') procedure, sugars in pulp from a Kamyr digester were determined by paper chromatography (9) and expressed as percentage of total carbohydrates (10). After correcting for glucose in galactoglucomannan, cellulose was also reported as percentage of total carbohydrates. Carbohydrate yield was then computed by Eq. (2):

$$100(Y\ cell/B) = Y\ carb \qquad (2)$$

where Y cell = yield of cellulose, % on o.d. wood,

B = cellulose, % of total carbohydrates,

Y carb = yield of carbohydrates, % on o.d. wood.

The value used for Y cell, determined from laboratory pulping, was 37%. Yield of noncarbohydrate residue, presumably lignin, was determined or estimated. Finally, it was added to carbohydrate yield to give total yield of unbleached pulp.

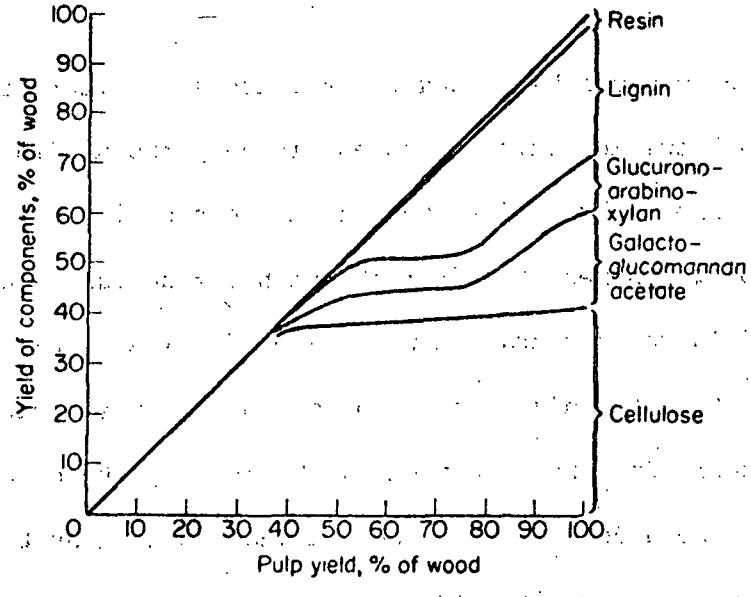

Figure 1. Dissolution of Sprucewood Components on Kraft Pulping. Yield of Components as a Function of Pulp Yield. From Rydholm (3)

A method similar to the Billeruds procedure has been used in the United States (11). Carbohydrates were determined by gas chromatography with inositol internal standard to give values for individual sugars and cellulose in pulp rather than sugar ratios. Lignin in pulp was estimated from kappa no. Steps in the procedure are outlined below:

$$\text{Lignin, \% on o.d. pulp} = (\text{kappa no.})(0.147) \quad (3)$$

$$\text{Total carbohydrates, \% on o.d. pulp: By analysis} \quad (4)$$

$$\text{Cellulose, \% on o.d. (softwood) pulp} = \text{Glucan} - \text{Mannan}/3 \quad (5)$$

$$\text{Cellulose, \% of carbohydrates} = (100)(\text{Eq. 5})/(\text{Eq. 4}) \quad (6)$$

$$\text{Yield of carbohydrates, \% on o.d. wood} = (100)(\text{Y cell})/(\text{Eq. 6}) \quad (7)$$

$$\text{Yield of lignin, \% on o.d. wood} \approx (\text{Eq. 3})(\text{Eq. 7})/100 \quad (8)$$

$$\text{Estimated total yield, \% on o.d. wood} = \text{Eq. 7} + \text{Eq. 8} \quad (9)$$

This procedure has been used to estimate yield improvements achieved in mill trials of a polysulfide pulping process in comparison with conventional kraft (11). Yield from polysulfide cooking was apparently about 2% higher than from kraft, most of which resulted from the higher glucomannan content of the pulp. Y cell values used in the computation were 37.0% for kraft and 37.5% for polysulfide. Thus far this technique has been used more for estimating yield differences than for determining absolute yields. Therefore, the exact values used for Y cell have not been considered to be critical as long as they do not change during pulping. For example, if a process change reduced the cellulose content of the carbohydrates from 82 to 78%, the improvement in carbohydrate yield estimated by Eq. (7) would be approximately 2.3% irrespective of whether the value of Y cell used in the calculation was 36 or 38%.

Recent studies in Scandinavia have employed carbohydrate determinations in a different manner for yield estimation (12,13). Pulps were produced in the laboratory using varied amounts of polysulfide and anthraquinone. Pulps from a particular cooking method were blended to achieve a kappa no. of exactly 60. The

TABLE I

CHANGES IN CELLULOSE CONTENT OF PULP DURING KRAFT COOKING OF LOBLOLLY PINE[a,c]

Cook Conditions					
Time to (hours)	Temp., °C	Time at (hours)	Yield[b]	Kappa[b] No.	Cellulose[b] in Pulp, % of wood
--	uncooked	--	100.0	--	42.0
1.0	140	--	79.9	--	38.4
1.5	170	0.00	67.8	139	35.9
--	170	0.25	63.6	127	36.5
--	170	0.50	61.2	125	37.1
--	170	1.0	54.2	81.1	36.6
--	170	1.5	50.6	53.7	36.2
--	170	2.0	48.1	44.7	35.5
--	170	3.0	47.8	24.6	35.4
--	170	4.0	46.2	21.5	36.3
--	170	6.0	46.0	13.6	36.4
--	170	8.0	44.6	14.2	35.5
--	170	10.0	44.0	13.0	34.8

[a]16.5% Effective alkali, 25% sulfidity, 5:1 liquor-to-wood ratio.
[b]Average of analyses of duplicate pulps.
[c]From Schroeder (6).

yields of these pulps were calculated and their sugar compositions determined. Plots of yield vs. mannan content at kappa no. 60 were constructed for each pulping process. Mill trials of the same processes were conducted in a Kamyr digester; the target kappa no. was 60. Pulp yields in the trials were estimated by determining mannan in the pulps and reading yield values from the yield vs. mannan plots based on laboratory cooks. This technique was reported not to be useful for conventional kraft cooks, because the pulps' sugar composition was essentially independent of pulp yield in the range of interest.

RESEARCH PLAN

High accuracy and precision of the carbohydrate determinations are essential for all uses of this method for estimating yield as well as for all other applications of carbohydrate analysis in pulping research. Consequently, precision of the carbohydrate analysis method is being studied first in this project.

Next to be investigated will be relationships between pulp yield and carbohydrate analyses for different pulping processes and wood species. The constancy and absolute magnitude of Y cell will be evaluated based upon pulps produced in the laboratory. Findings will be applied to mill-scale pulping processes. Potential difficulties in mill use of the procedure will be considered, including variations in the wood supply, obtaining representative samples for analysis, and nonuniform pulping in the digester.

PRECISION OF THE CARBOHYDRATE METHOD FOR YIELD ESTIMATION

COMPARISON OF METHODS OF PULP YIELD ESTIMATION BASED ON CARBOHYDRATE ANALYSES

A kraft pulp was prepared in the laboratory from loblolly pine. Kappa no. was 34.0, and pulp yield, established by weighing chips and pulp, was 46.8%. Carbohydrate analyses, using the method of Borchardt and Piper (1), were performed 13 times on different days. Estimated pulp yields were computed using Eq. (1) (Method A) and Eq. (3)-(9) (Method B); a Y cell value of 37.0 was used in the calculations. Data are shown in Tables II-IV. The poor agreement between estimated yields and actual yield suggests either that Y cell = 37.0 was inappropriate for this pulp or that there was an error in the determination of actual pulp yield. Using Eq. (1), an estimated yield of 48.4% may be computed from the cellulose content of the pulp and Y cell = 36.1 from Schroeder's data (Table I). This suggests that the measured pulp yield, 46.8%, may have been erroneously low. However, the apparent error in actual pulping yield measurement should not affect the following discussion of method precision.

Standard deviation values for estimated pulp yields provide an indication of how far apart estimated yields must be before they can be considered significantly different. The standard deviation for Method A given in Table IV is 0.57; thus duplicate carbohydrate analyses must indicate estimated yields differing by 1.27% before the difference is considered significant at the 95% level*. Method B, with a lower standard deviation, would seem to be able to distinguish between pulps having yields differing by 0.61%.

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*$\bar{X}_a - \bar{X}_b = ts \sqrt{1/n_a + 1/n_b}$

$\bar{X}_a - \bar{X}_b = (2.23)(0.57) \sqrt{1/2 + 1/2} = 1.27$

TABLE II

KRAFT PULP ANALYSIS

Date	Glucan, % of o.d. pulp	Mannan, % of o.d. pulp	Cellulose, % of o.d. pulp[a]	Xylan, % of o.d. pulp	Galactan, % of o.d. pulp	Araban, % of o.d. pulp
3-28-80	76.6	7.5	74.1	8.5	1.2	0.7
3-28-80	77.4	7.4	74.9	8.5	1.1	0.7
3-28-80	76.8	7.3	74.4	8.2	1.1	0.6
3-31-80	78.7	7.7	76.1	8.6	1.5	0.7
4-3-80	76.0	7.3	73.6	8.2	1.5	0.8
4-4-80	76.3	7.2	73.9	8.1	1.3	0.6
4-4-80	76.5	7.4	74.0	8.2	1.2	0.7
4-4-80	77.4	7.3	75.0	8.3	1.1	0.7
4-4-80	75.7	7.5	73.2	8.1	1.3	0.7
4-7-80	77.4	7.2	75.0	8.4	1.1	0.7
4-7-80	77.5	7.3	75.1	8.1	1.1	0.6
4-7-80	77.7	7.2	75.3	8.6	1.0	0.6
4-7-80	78.2	7.4	75.7	8.1	1.1	0.6

[a] Equation (5).

Insight into the reasons for the higher standard deviation of Method A compared with Method B is provided by considering Eq. (1) in detail. The factor 100 may be removed from Eq. (1) by expressing C as a fraction of the pulp rather than a percentage:

$$Y_t = Y \text{ cell}/C \qquad (1)$$

If the pulp is composed only of cellulose, hemicellulose, and lignin,

TABLE III

RESULTS COMPUTED FROM CARBOHYDRATE DATA

Date	Total Carbohydrate (TC), % of o.d. pulp	Lignin in Pulp, %[a]	Cellulose, % of TC[b]	Yield of Carbohydrate[c]	Yield of Lignin[d]	Yield of Pulp[e]	Yield of Pulp[f]
3-28-80	94.5	5.5	78.4	47.2	2.75	49.9	49.6
3-28-80	95.1	4.9	78.8	47.0	2.42	49.4	49.4
3-28-80	94.0	6.0	79.1	46.8	2.98	49.7	49.1
3-31-80	97.2	2.8	78.3	47.2	1.36	48.6	49.6
4-3-80	93.8	6.2	78.5	47.1	3.12	50.3	49.5
4-4-80	93.5	6.5	79.0	46.8	3.25	50.1	49.1
4-4-80	94.0	6.0	78.7	47.0	3.00	50.0	49.4
4-4-80	94.8	5.2	79.1	46.8	2.56	49.3	49.1
4-4-80	93.3	6.7	78.4	47.2	3.39	50.5	49.6
4-7-80	94.8	5.2	79.1	46.8	2.56	49.3	49.1
4-7-80	94.6	5.4	79.4	46.6	2.66	49.3	48.9
4-7-80	95.1	4.9	79.2	46.7	2.41	49.1	49.0
4-7-80	95.4	4.6	79.4	46.6	2.25	48.9	48.9

[a] 100-TC.
[b] Eq. (6)
[c] Eq. (7)
[d] (Y cell)(Lignin in Pulp)/Cellulose in Pulp
[e] Eq. (1) (Method A)
[f] Eq. (3)-(9) (Method B)

$$C = C_e/(C_e + H + L) \tag{10}$$

where C_e = cellulose in pulp, g,

H = hemicellulose in pulp, g, and

L = lignin in pulp, g.

Substituting Eq. (10) in Eq. (1):

$$Y_t = (Y\ cell)(C_e + H + L)/C_e \tag{11}$$

Separating Eq. (11) into two parts:

$$Y_t = (Y\ cell)(C_e + H)/C_e + (Y\ cell)(L)/C_e \tag{12}$$

The $(Y\ cell)(C_e + H)/C_e$ term represents carbohydrate yield; it is essentially identical with Eq. (7). $(Y\ cell)(L)/C_e$ represents lignin yield.

Estimation of pulp yield via Method A employs only carbohydrate data. Lignin, assumed to be the only noncarbohydrate material in the pulp, may be determined by difference. In any analysis, an increase in the percentage of the material determined implies a reduced percentage of everything else in the sample. Thus, if there is a positive error in the carbohydrate analysis, lignin (by difference) must reflect a compensating negative error. This would cause substantial changes in the L/C_e ratio and in the computed lignin yield.

Cellulose is by far the predominant carbohydrate in the pulp studied. An error in C_e will be matched by a similar error in $C_e + H$. Thus, errors in C_e will have little effect on the $(C_e + H)/C_e$ ratio and on the estimated carbohydrate yield.

TABLE IV

PRECISION OF RESULTS

Measurement	Average, %[a]	Standard Deviation[a]	Variance
Glucan	77.1	0.87	0.757
Mannan	7.4	0.15	0.022
Xylan	8.3	0.20	0.040
Galactan	1.2	0.16	0.026
Araban	0.7	0.07	0.005
Total carbohydrate	94.6	1.01	1.02
Cellulose, % of T.C.	78.9	0.39	0.152
Pulp Yield[b]	49.6	0.57	0.325
Pulp Yield[c]	49.2	0.23	0.053
Carbohydrate yield[d]	46.9	0.22	0.048
Lignin yield[e]	2.67	0.53	0.281

[a] Based on 13 trials on a kraft pulp.
[b] Computed using Eq. (1) (Method A).
[c] Computed using Eq. (3)-(9) (Method B).
[d] Eq. (7).
[e] (Y cell)(lignin in pulp)/cellulose in pulp.

For each of the carbohydrate analyses in Table II lignin values have been determined from total carbohydrates by difference and are recorded in Table III. Also in Table III are carbohydrate and lignin yields computed using the two parts of Eq. (12), with lignin values obtained by difference. Because they are derived from the same experimental data used in a rearranged version [Eq. (12)] of the same basic equation [Eq. (1)], the variances of the carbohydrate and lignin yield values when summed equal the variance of pulp yield estimated by Method A, as shown in

Table IV. The variance of the lignin yield accounts for most (85%) of the variance of the pulp yield. Thus, the poorer precision of yields estimated by Method A, in contrast with Method B, appears to result from basing the estimate on determinations of only one class of components — the carbohydrates — in a multicomponent sample.

Pulp yield estimation by Method B uses independent determinations of carbohydrates and lignin. The similarity between the variances of the carbohydrate yield and the pulp yield data in Table IV suggests that the precision of the carbohydrate determinations controls the precision of yield estimates by Method B. Improvements in the carbohydrate method should therefore bring about improvements in yield estimation.

The variation in lignin yield estimates used in Method B may have been unrealistically low, because the pulp's kappa no. was measured only once in this investigation. A better indication of lignin yield variation would have resulted if kappa no. had been measured each time a carbohydrate analysis was performed. Because these measurements were not made, estimates of lignin yield variation must be based on published data on the precision of the kappa no. determination. In TAPPI Test Method T 236 os-76, the average repeatability of the kappa no. test is reported to be 1.2% for kappa no. between 20 and 190. Variance of lignin yields, estimated from kappa no. repeatability as shown in Appendix I, appeared to be small compared with the variance of carbohydrate yields.

ACCURACY AND PRECISION OF THE GAS CHROMATOGRAPHIC METHOD FOR CARBOHYDRATES

Derivatized carbohydrates from one of the kraft pulp samples were injected into the gas chromatograph nine consecutive times to establish the precision of the

gas chromatographic analysis. Day-to-day variation was avoided by performing all nine injections on the same day. Data are in Table V. A comparison of the standard deviations in Table V with those for the whole determination in Table IV suggests that GC analysis contributed significantly to the variation of the complete method. This impression will be tested more rigorously by including replicate injections in a future factorial experiment. Use of an internal standard in the sample should have compensated for variations in manual injections into the GC. Thus, the variations in Table V should be inherent in the instrumental portion of the analysis. Integration and calculations were performed by a Hewlett-Packard 3385A data system connected to a Packard model 417 gas chromatograph.

TABLE V

PRECISION OF GAS CHROMATOGRAPHIC ANALYSIS

Test	Glucan, %	Mannan, %	Xylan, %	Galactan, %	Araban, %
1	77.4	7.5	8.2	1.5	0.7
2	77.8	7.4	8.4	1.0	0.7
3	77.5	7.3	8.3	1.0	0.7
4	77.7	7.3	8.2	1.1	0.6
5	77.7	7.4	8.2	1.1	0.6
6	77.7	7.3	8.1	1.2	0.6
7	77.4	7.3	8.2	1.1	0.7
8	77.8	7.3	8.1	1.0	0.6
9	77.1	7.3	8.1	1.2	0.6
Average %	77.6	7.3	8.2	1.1	0.6
Standard deviation	0.24	0.09	0.10	0.16	0.07

Calibration of the gas chromatographic method for carbohydrates has also been found to be a potential source of error in this procedure for yield estimation. Pure monosaccharides were originally specified for method calibration. However, recent analyses of monosaccharides with and without hydrolysis have suggested that the acid hydrolysis converts about 5% of the mannose standard into glucose. In addition, "pure" monosaccharides from different vendors are not always the same. These problems might be avoided by use of a standard pulp for calibration in all laboratories performing this determination. Such a pulp is now available at the Institute.

Since publication of the Borchardt and Piper method for carbohydrate analyses in 1970 (1), a number of pieces of equipment and procedures have been found to be valuable in assuring the accuracy and precision of the analysis. They are listed below:

(1) Add inositol internal standard as a solution (10.0 mL = 100 mg) prior to secondary hydrolysis.

(2) For better control of secondary hydrolysis, place samples in a preheated autoclave.

(3) Use a rotary evaporator that can take the reduced sugars and the alditol-acetates to dryness in 10-15 minutes at 70°C. (Model 5101 Rotary Evaporator, Scientific Manufacturing Industries, 1399 64th Street, Emeryville, CA 94609).

(4) Connect the rotary evaporator to a recycling water aspirator instead of an aspirator operating on a municipal water supply. (Pope Aqua-Jet Aspirator, Pope Scientific Inc., Menominee Falls, WI 53051).

(5) Use Baker's reagent grade acetic anhydride. Other grades give peaks which interfere with xylose on the chromatogram.

(6) Use the column packing originally recommended, ECNSS-M. In spite of advances in column packings, this still gives the best separation.

(7) Use an electronic data system for integration of peak areas.

FUTURE WORK

Pulps will be produced in the laboratory over a range of accurately measured yield levels, from different wood species, and utilizing different pulping processes, process variables, and additives such as anthraquinone. Carbohydrate, kappa no., and Klason lignin determinations will be performed on these pulps. Results will be used to document the magnitude and constancy or variability of Y cell.

If Y cell is found to have a low variability, the yield estimation procedure will then be tested by comparing estimated yields with actual yields obtained in capsule cooks in batch digesters. The utility of this procedure for estimating yields in continuous digesters will be studied indirectly, such as by demonstrating the sensitivity of estimated yields to changes in the kappa no. of pulps made in the mill. Comparisons will also be made with other methods of estimating yield in the mill, such as yield vs. kappa no. curves.

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APPENDIX I

ESTIMATION OF VARIATION OF LIGNIN YIELD BASED UPON KAPPA NO. REPEATABILITY

In TAPPI T 236 os-76 the average repeatability of the kappa no. test is reported to be 1.2% for kappa no. between 20 and 190. For a pulp with kappa no. 34, 1.2% repeatability is (1.2)(34)/100 = 0.408 kappa no. In TAPPI T 1206 os-69 repeatability (within a laboratory) is defined as 2.77 times the standard deviation of a test result. Thus, the standard deviation of a kappa number test (at 34 kappa) would be 0.408/2.77 = 0.147.

The relative standard deviation for kappa number at 34 kappa = 0.147/34 = 0.00433. Lignin in pulp computed from kappa no. times the constant 0.147 would have the same relative standard deviation, 0.00433.

From the data in Table IV, the relative standard deviation for carbohydrate yield can be computed to be 0.22/46.9 = 0.00469. According to Eq. (8), lignin yield can be approximated by multiplying lignin in pulp by carbohydrate yield. The random relative error of a quantity computed as a product or quotient is the square root of the sum of the squared relative errors of the terms in the computation (14). Thus, the relative error of lignin yield =

$$((0.00433)^2 + (0.00469)^2)^{1/2} = 0.00638$$

For a lignin yield of 2.35%, the random absolute error would be (2.35)(0.00638) = 0.015%. If this may be considered to be an estimate of the standard deviation of lignin yield, the variance would be 0.000225. This appears insignificant compared with the variance of carbohydrate yield shown in Table IV.